

The efficiency of the ILUV oxidation method for organic nitrogen analysis

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Abstract A new approach to measure dissolved organic nitrogen in fresh waters was developed as an alternative to more expensive techniques, such as traditional UV oxidation and high temperature oxidation and to more labor-intensive techniques that produce hazardous by-products, such as persulfate oxidation. The new approach, called the individual lamp UV (ILUV) method, was applied to model compounds and humic substances. For the selected model compounds, ethylenediaminetetraacetic acid, glycine and urea, the ILUV oxidation method resulted in 93% to 114% recoveries. In the case of humic substances, the recoveries ranged from 100% to 126%. It was found that the ILUV method is a simple, cheap and promising method for determination of DON in natural waters.

Keywords Dissolved organic nitrogen; DON; humic substances; natural organic matter; nitrogenous organic compounds; NOM; UV oxidation; water treatment

Introduction

Total nitrogen (TN) in natural waters consists of ammonia (NH_3), nitrate (NO_3^-), nitrite (NO_2^-), and nitrogenous organic compounds (NOCs). Dissolved organic nitrogen (DON) is the fraction of NOCs that passes through a 0.45-micron filter. Westerhoff and Marsh (2002) reported that DON in fresh waters typically constitutes a smaller portion of dissolved organic matter (DOM), approximately 0.5–10% by weight. This is consistent with the previous reports that humic substances comprised 0.2 to 6% nitrogen (Thurman, 1985; Karanfil, 1995; Kieber *et al.*, 1999). Westerhoff and Marsh (2002) also reported that DON is commonly the dominant form (>50%) of total dissolved nitrogen (TDN) in fresh waters that are not significantly impacted by human activities.

DON in fresh waters originates from natural (e.g. humic substances, algal growth, proteins, peptides, and amino acids), agricultural (e.g. pesticides and fertilizers) and industrial (e.g. amines and nitrophenols) sources. The presence and concentration of DON in natural waters are of interest for various reasons. DON components serve as precursors for various disinfection by-products (e.g. haloacetonitriles, nitrosamines) that are suspected or probable human carcinogens. They exert a high chlorine demand and form organic chloramines that do not have disinfection power. They may also interfere with the inorganic chloramine measurement. A decrease in the DOC (dissolved organic carbon)/DON ratio indicates an increase in allochthonous DON entering the aquatic system from external sources and/or occurrence of algae blooms.

There is no direct method to measure DON in natural waters. DON is quantified by oxidizing the organic nitrogen to its inorganic forms such as nitrate and ammonia, and subsequently measuring these inorganic nitrogen species. UV oxidation, persulfate oxidation, and high temperature oxidation are commonly used to oxidize DON. Analytical methods including ion chromatography, UV spectroscopy and ion-selective electrode measurements are commonly used to quantify the resulting inorganic nitrogen species. Both the oxidation and analytical methods require expensive analytical equipment.

The objectives of this research were to: 1) develop a simple and inexpensive method

based on UV oxidation to determine DON in fresh water samples, 2) investigate the ability of the second derivative UV absorbance (2DUV) method to quantify NO_3^- , and 3) apply the newly developed method to the oxidation of selected model nitrogenous compounds and humic substances. The new method, referred to here as the individual lamp UV oxidation (ILUV) method, utilizes UV irradiation but not in the method traditionally reported in the literature. ILUV uses less powerful and less expensive pen-sized UV lamps, and the lamp is directly submerged in the sample to be oxidized. Multiple lamps are needed in order to oxidize multiple samples. One UV lamp and required power supply cost less than five hundred dollars. The ILUV method incorporates UV spectroscopy to quantify both nitrate and ammonia in the oxidized samples. Therefore, the method requires a UV spectrophotometer, which is less expensive than an ion chromatograph and more commonly found in water treatment plants and other chemistry laboratories.

Materials and methods

Experimental method

The experimental method described here is the result of several months of optimizing. The evolution of the method is described in detail elsewhere (Smith, 2003). Only the final method (i.e. Individual Lamp UV Oxidation (ILUV)) is presented here. The experimental configuration is shown in Figure 1.

Each oxidation requires approximately 125 mL of solution. A serum bottle capped with 3/8" punched septa is filled completely with the sample. A syringe (plunger removed) is placed anywhere in the exposed section of the septa on the capped serum bottle to allow the solution to be displaced. With the syringe in place, the UV lamp (Part #: 90-0004-07, UVP, Inc. Upland, CA) is slowly inserted through the cap and septa until the lamp tip touches the bottom of the serum bottle. The bottle and the lamp are wrapped with aluminum foil. A fan is directed at the apparatus to cool the handle of the lamp and allow its safe handling after oxidation. The power supply for the UV lamp and the fan is turned on and the sample is oxidized for 48 hours. The oxidized sample is filtered using a prewashed membrane filter (Supor® 0.45 μm , Gelman Sciences, Ann Arbor, MI) to remove small pieces of the septa that may enter the solution as the lamp is removed. The filtrate is analyzed for pH, ammonia, and nitrate.

Analytical methods

In this study, several analytical methods were used to optimize and validate the performance of the ILUV method. The total nitrogen (TN) and organic carbon (TOC) in

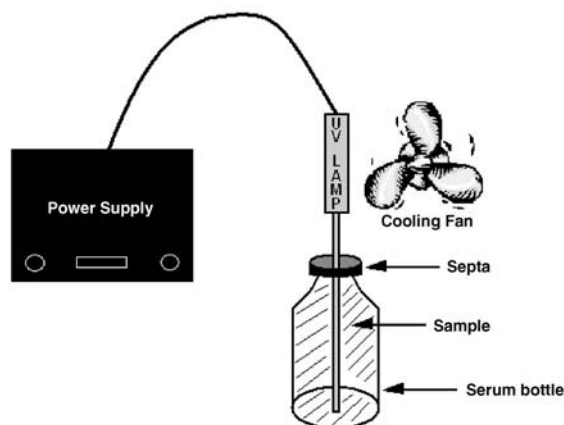


Figure 1 ILUV system

each sample were measured using a high temperature combustion TOC/TN analyzer (TOC-V, TNM-1, Shimadzu Corporation, Japan) before and after oxidation. In each oxidized and filtered sample, nitrate was quantified with the 2DUV and ion chromatography (IC), while ammonia was quantified using an ion-selective probe and according to Standard Method (SM) 4500-NH₃ F. Therefore, these analyses allowed for the determination of the total nitrogen in oxidized samples in five different ways: i) high temperature oxidation (HTO), ii) 2DUV and NH₃ probe, iii) 2DUV and SM 4500, iv) IC and NH₃ probe, v) IC and SM 4500. Experiments showed that formation of nitrite was negligible in the samples.

The 2DUV method has been described in the literature as an effective method for determining nitrate concentrations (Eckford and Fedorak, 2002; Ferree and Shannon, 2001; Holm *et al.*, 1997; Bachmann and Canfield, 1996; Crumpton *et al.*, 1992; Simal *et al.*, 1985). Detection limits of this method have been reported to be as low as 5 ppb NO₃⁻ (Crumpton *et al.*, 1992) to as high as 100 ppb NO₃⁻ (Holm *et al.*, 1997). The 2DUV method works on the premise that NO₃⁻ strongly absorbs UV radiation in the wavelength range of 200–230 nm. In this study, the second derivative value at 224 nm was used to determine the NO₃⁻ concentration. The UV scans were performed using a Beckman Model DU-640 Spectrophotometer. Because of the signal to noise ratio associated with the UV scans, forty-point adjacent averaging was used to smooth the data. A set of nitrate standards between 50–4,000 ppb was analyzed side-by-side with the 2DUV method and IC. The results correlated well, giving a slope of 0.996 and linear regression coefficient (R²) of 0.998. This finding is consistent with results from Ferree and Shannon (2001), who reported no significant difference between results from IC and the 2DUV method. The impacts of NOM (0.5 to 10 mg DOC/L) and bromide (0.5 to 4 mg/L) concentrations on the 2DUV results were also investigated. No interference of NOM and bromide on the 2DUV results was found (Smith, 2003). This was also consistent with the reports by Crumpton *et al.* (1992) and Ferree and Shannon (2001). The method detection limit (MDL) for the 2DUV method was determined to be 50 ppb according to Standard Method 1030 E (APHA, WEF and AWWA, 1999). After performing several measurements, a practical quantification limit (PQL) was set at two times the MDL (i.e. 100 ppb NO₃⁻). A Dionex ion chromatography (IC) unit consisting of an AS50 autosampler, an AS50 chromatography compartment, an ED40 electrochemical detector, and a GP50 gradient pump was also used to measure nitrate. The PQL of the method was 50 ppb as NO₃⁻-N. Ammonia in samples was quantified with an Orion ammonia electrode (Model 95-12) and according to Standard Method 4500-NH₃ F phenate method. The PQLs for both methods were 50 ppb as NH₃-N.

Nitrogenous organic compounds

The following NOCs were oxidized according to the ILUV oxidation method: glycine (E.M. Science, OmniPur), ethylenediaminetetraacetic acid (EDTA) (J.T. Baker, Technical Grade), urea (Fisher Scientific, A.C.S), and several humic substances. Glycine, EDTA and urea are referred to as “model compounds” in this research. They were selected because there is appreciable information in the literature on the percent recoveries of these compounds using the traditional DON quantification techniques. In addition, glycine is one of the most commonly occurring amino acids in natural waters (Ram and Morris, 1980; Thurman, 1985; Chin and Barret, 2000). All humic substances were acquired from the International Humic Substances Society (IHSS, St. Paul, Minnesota) (Table 1). These humics were selected because of the range of their nitrogen contents.

Results and discussion

Model NOCs

The model compounds analyzed included EDTA, glycine, and urea. Various dilutions of

Table 1 IHSS humic substances tested in this study

IHSS Cat. No.	Humic description	%N ^a	%C ^a
1R106H	Summit Hill Soil HA Reference (SHSHR)	5.13%	54.00%
1S102H	Elliott Soil Humic Acid Standard (ESHAS)	4.14%	58.13%
1S103H	Pahokee Peat Humic Acid Standard (PPHAS)	3.69%	56.37%
1S101H	Suwannee River Humic Acid Standard (SRHAS)	1.19%	52.55%
1R108N	Nordic Reservoir NOM (RO isolation) (NRN)	1.10%	53.17%

a – %N and %C as reported by supplier of humics, International Humic Substances Society, St. Paul, MN, USA

each model compound were made using distilled and deionized water (DDI) and the respective compound. Table 2 shows the diluted compound concentrations as total nitrogen (TN) and total organic carbon (TOC) in two forms: (i) theoretical: based on calculation using the weight and molecular structure of the compound, and (ii) measured: based on the measured TN and TOC values using the TOC/TN analyzer (i.e. HTO method). In general, the theoretical and measured values were in good agreement, indicating that the HTO method was effective in measuring TN in the samples.

The TN concentrations measured before and after ILUV oxidation for three model NOCs are shown in Table 3. Since there was no inorganic nitrogen present in these solutions before oxidation, the measured TN values were also equal to dissolved organic

Table 2 TN and TOC concentration for model compounds

Name of compound	TN concentration before oxidation (ppm N)		TOC concentration before oxidation (ppm C)	
	Theoretical ^a	TN ^b	Theoretical ^a	TOC ^b
EDTA	0.26	0.22	1.10	0.83
	0.51	0.51	2.19	2.14
Urea	0.25	0.24	0.11	0.24
	0.50	0.43	0.21	0.22
Glycine	0.51	0.46	0.88	0.85

a – Total nitrogen and total carbon as determined theoretically from molecular structure and weight of compound

b – TN and TOC as determined from the TOC/TN analyzer

Table 3 ILUV method results for model compounds

NOC	TN ^a before oxidation (ppm N)	TN concentration (ppm N) and % recovery after (ILUV) oxidation ^b				
		HTO ^a	2DUV+Probe	2DUV+SM 4500	IC + Probe	IC+ SM 4500
EDTA	0.22	0.16 (6, 0.02) [74%]	0.17 (6, 0.02) [75%]	0.22 (6, 0.02) [97%]	0.16 (6, 0.04) [71%]	0.21 (6, 0.04) [94%]
	0.51	0.41 (6, 0.01) [81%]	0.44 (6, 0.01) [87%]	0.47 (6, 0.01) [93%]	0.45 (6, 0.01) [89%]	0.49 (6, 0.01) [96%]
Urea	0.24	0.24 (6, 0.02) [99%]	0.23 (6, 0.004) [94%]	0.25 (6, 0.003) [101%]	0.23 (6, 0.004) [93%]	0.24 (6, 0.004) [100%]
	0.43	0.45 (6, 0.01) [106%]	0.46 (6, 0.003) [107%]	0.49 (6, 0.003) [114%]	0.45 (6, 0.005) [106%]	0.48 (6, 0.005) [112%]
Glycine	0.46	0.36 (6, 0.01) [78%]	0.44 (6, 0.03) [95%]	0.48 (6, 0.01) [103%]	0.44 (6, 0.04) [95%]	0.47 (6, 0.01) [102%]
Average recovery of all model compounds		88%	92%	102%	91%	101%

a – Total nitrogen (TN) as determined from the high temperature oxidation TN Analyzer

b – For each oxidized sample, the values in the first line represent the average total nitrogen based on the respective analysis. The values provided in the second line, (x, x.xxx) [xx%] are the number of samples analyzed (x), the 95% confidence interval (x.xxx) and the recovery [xx%], respectively. The recovery is the ratio of the average TN after oxidation relative to TN before oxidation

nitrogen. In order to determine the degree of oxidation of model NOCs by the individual UV lamps, the TOC concentrations following oxidation were also measured. The results were below the detection limit of the TOC measurement (0.2 mg/L), indicating that model compounds were completely oxidized during UV oxidation.

The average percent recovery calculated for each set of analyses ranged between 88% and 101%. The ILUV method that incorporates 2DUV+SM 4500 or IC+SM 4500 produced the best results. It was found that at low organic nitrogen concentrations, the ammonia determination using the ammonia probe was less accurate than the SM 4500. As a result, lower recoveries were calculated for lower NOC concentrations when ammonia values were obtained from the ammonia probe. Good recoveries obtained using 2DUV and SM 4500 were promising since these two techniques use a UV spectrophotometer for determining nitrate and ammonia, respectively. The obtained recoveries for each model compound with the ILUV method that incorporates 2DUV+SM 4500 were compared with those reported in the literature (Table 4). This comparison indicated that the ILUV method performance was comparable to other traditional methods that have been used to measure NOCs in natural waters.

Humic substances

The humics were acquired in a lyophilized form. The solid samples were initially analyzed using a high temperature combustion N analyzer to verify %N contents (Table 5). Some variability observed between the %N numbers reported by IHSS and measured in this study was expected, provided that IHSS values represent the average of a number of measurements from a large stock. Each humic was then dissolved in DDI water by raising the pH to 10 with sodium hydroxide. Hydrochloric acid was then added to the solution to neutralize the pH. Each humic stock was analyzed using the TOC/TN analyzer (i.e. measured values in Table 5). As for model NOCs, the theoretical and measured TOC/TN values for each humic were compared. In general the measured and theoretical values were relatively similar, however some differences were also observed. These differences were attributed to two factors: (i) The organic carbon contents of the samples used in the experiment were not measured, therefore for the calculation of theoretical TOC values the elemental analysis results provided by IHSS were used, and (ii) some analytical errors (e.g. weighing and dissolving of the samples, adjustment of the volumes, and dilution of samples) in the preparation of the samples may have impacted the measured values. Since the carbon content is significantly higher than the nitrogen content for humics, the impact of such analytical errors would be higher on the measured TOC values than the TN values.

The TN concentrations measured before and after ILUV oxidation for five humic substances are shown in Table 6. As for model NOC experiments, there was no inorganic nitrogen present in these solutions before oxidation, therefore the measured TN values were also equal to dissolved organic nitrogen. In order to determine the degree of oxidation of the humic substances by the individual UV lamps, the TOC concentrations following oxidation were also measured. The results indicated that the degree of oxidation during the ILUV method (i.e. 48 hr of oxidation) depended on initial humic substance concentration. About 90% of initial TOC was oxidized when the initial concentration was 5 ppm TOC or lower. The concentration range of 1 to 4 mg/L is representative of typical TOC values in drinking water sources in the United States (Oxenford, 1996). Therefore, it appears that the ILUV method will be able to oxidize organic materials in most of the fresh waters in the United States. However, for higher initial TOC concentrations, longer oxidation times or addition of an oxidizing agent may be necessary. The average percent recovery calculated for each set of analyses ranged between 80% and 112%. As for model NOCs, the ILUV method that incorporates 2DUV+SM 4500 showed good recoveries. The obtained recoveries with the

Table 4 Comparison of recoveries for NOCs tested in this study with those reported in literature

Conc. (ppm N)	UREA		Reference	EDTA		Conc. (ppm N)	Recovery (%)	Reference	Conc. (ppm N)	Recovery (%)	GLYCINE		Reference
	Recovery (%)	Method		Recovery (%)	Method						Method		
0.24	101	ILUV	This Research	97	ILUV	0.22	97	This research	0.46	103	ILUV	This research	
0.43	114	ILUV	This Research	93	ILUV	0.51	93	This research	0.14	85	UV	Bronk <i>et al.</i> , 2000	
0.07	101	UV	Bronk <i>et al.</i> , 2000	88	UV	0.14	88	Bronk <i>et al.</i> , 2000	0.56	96	UV	Walsh, 1989	
0.14	83	UV	Walsh, 1989	103	UV	0.28	103	Walsh, 1989	1.12	55	UV	Bronk <i>et al.</i> , 2000	
0.14	98	UV	Armstrong and Tibbitts, 1968	77	UV	0.56	77	Bronk <i>et al.</i> , 2000	0.14	97	UV w/ PO	Bronk <i>et al.</i> , 2000	
0.35	96	UV	Bronk <i>et al.</i> , 2000	96	UV	0.56	96	Walsh, 1989	1.12	95	UV w/ PO	Bronk <i>et al.</i> , 2000	
0.56	73	UV	Walsh, 1989	93	UV w/ PO ^a	0.14	93	Bronk <i>et al.</i> , 2000	0.14	99	UV w/ PO	Bronk <i>et al.</i> , 2000	
1.05	76	UV	Bronk <i>et al.</i> , 2000	95	UV w/ PO	0.56	95	Bronk <i>et al.</i> , 2000	0.58	100	PO	Raimbault <i>et al.</i> , 1999	
NR	102	UV	Cornell and Jickells, 1999	14	PO ^b	0.14	87	Bronk <i>et al.</i> , 2000	1.12	97	PO	Bronk <i>et al.</i> , 2000	
0.04	97	UV w/ PO	Bronk <i>et al.</i> , 2000	89	PO	0.56	89	Bronk <i>et al.</i> , 2000	NR	100	PO	D'Elia <i>et al.</i> , 1977	
0.07	81	UV w/ PO	Bronk <i>et al.</i> , 2000	100	PO	NR	100	D'Elia <i>et al.</i> , 1977	0.14	94	HTO	Bronk <i>et al.</i> , 2000	
1.05	97	UV w/ PO	Bronk <i>et al.</i> , 2000	74	HTO	0.22	74	This research	0.46	78	HTO	This research	
0.07	99	PO	Bronk <i>et al.</i> , 2000	81	HTO	0.51	81	This research	0.56	100	HTO	Walsh, 1989	
0.35	106	PO	Bronk <i>et al.</i> , 2000	102	HTO	0.28	102	Walsh, 1989	1.12	77	HTO	Bronk <i>et al.</i> , 2000	
1.05	100	PO	Bronk <i>et al.</i> , 2000	58	HTO	0.56	58	Bronk <i>et al.</i> , 2000					
1.17	100	PO	Raimbault <i>et al.</i> , 1999	101	HTO	1.12	101	Bronk <i>et al.</i> , 2000					
NR	87	PO	Cornell and Jickells, 1999	96	HTO	1.4	96	Walsh, 1989					
NR	100	PO	D'Elia <i>et al.</i> , 1977	93	HTO	3.92	93	LePoupon <i>et al.</i> , 1997					
0.07	97	HTO	Bronk <i>et al.</i> , 2000	≥100	HTO	NR	≥100	Bronk <i>et al.</i> , 2000					
0.14	100	HTO	Walsh, 1989					Hopkinson <i>et al.</i> , 1993					
0.24	99	HTO	This Research										
0.35	96	HTO	Bronk <i>et al.</i> , 2000										
0.43	106	HTO	This Research										
0.56	102	HTO	Walsh, 1989										
1.05	97	HTO	Bronk <i>et al.</i> , 2000										
1.40	84	HTO	LePoupon <i>et al.</i> , 1997										

ILUV: Individual UV Lamp oxidation; UV: UV oxidation; PO: persulfate oxidation; HTO: high temperature oxidation; w/PO: with persulfate oxidation

Table 5 TN and TOC concentration for humics

Humic	% N		TN (ppm N)		% C		TOC (ppm TOC)	
	IHSS ^a	CU ^b	Theoret. ^c	Measured ^d	IHSS ^a	CU ^b	Theoret. ^c	Measured ^d
SHSHR	5.13%	4.67%	0.46	0.31	54.00%	NE	4.56	3.14
ESHAS	4.14%	3.63%	0.45	0.40	58.13%	NE	6.15	5.28
PPHAS	3.69%	3.33%	0.45	0.41	56.37%	NE	6.57	7.18
SRHAS	1.19%	NE	0.50	0.31	52.55%	NE	18.93	19.88
NRN	1.10%	0.79%	0.36	0.26	53.17%	NE	20.72	10.26 ^e

NE – not evaluated

a – %N as reported by supplier of humics, International Humic Substances Society, St. Paul, MN, USA

b – %N as reported by the Agriculture Service Laboratory, Clemson Extension, Clemson University (CU), Clemson, SC, USA

c – Total nitrogen as calculated based on humic addition and CU %N when available, otherwise, IHSS %N and %C

d – Total nitrogen as quantified by TOC/TN analyzer, Clemson University, Clemson, SC, USA

e – Error in the preparation of the target stock

Table 6 ILUV method results for humic substances

Humic	TN ^a before oxidation (ppm N)	TN concentration (ppm N) and % recovery after (ILUV) oxidation ^b				
		HTO ^a	2DUV+ Probe	2DUV+ SM 4500	IC + Probe	IC+ SM 4500
SHSHA	0.31	0.34 (6, 0.01) [108%]	0.32 (6, 0.02) [104%]	0.39 (6, 0.03) [126%]	0.32 (6, 0.02) [104%]	0.39 (6, 0.03) [125%]
ESHAS	0.40	0.41 (6, 0.01) [102%]	0.34 (6, 0.01) [86%]	0.43 (6, 0.02) [107%]	0.34 (6, 0.01) [84%]	0.42 (6, 0.03) [105%]
PPHAS	0.41	0.47 (4, 0.03) [114%]	0.39 (4, 0.03) [95%]	0.45 (4, 0.02) [109%]	0.37 (4, 0.03) [89%]	0.42 (4, 0.02) [103%]
SRHAS	0.31	0.27 (6, 0.02) [88%]	0.32 (6, 0.01) [103%]	0.37 (6, 0.01) [120%]	0.19 (6, 0.03) [62%]	0.25 (6, 0.04) [79%]
NRN	0.26	0.27 (4, 0.02) [105%]	0.21 (4, 0.01) [83%]	0.26 (4, 0.01) [100%]	0.16 (4, 0.04) [61%]	0.20 (4, 0.01) [78%]
Average recovery of all humics		103%	94%	112%	80%	98%

a, b: Same as at the footnote of Table 3

ILUV method were compared with some of those reported for other humics in the literature (Smith, 2003). In general, the performance of the ILUV method was very comparable to the other methods.

Conclusions

The important findings from this study are

- A new, simple, and inexpensive method, called ILUV, which incorporates UV oxidation and UV spectrophotometry for nitrate and ammonia measurements, was developed to determine DON in fresh water samples.
- It was shown that the second derivative UV method for measuring nitrate yields comparable results to those obtained from ion chromatography. No interference of NOM (0.5 to 10 mg DOC/L) and bromide (0.5 to 4 mg/L) on the second derivative UV results was found.
- When the ILUV method was applied to selected model compounds, EDTA, urea and glycine, the recoveries ranged from 93% to 114%, which was comparable to those obtained by using other techniques (e.g. traditional UV, persulfate oxidation and high temperature oxidation) for measuring these compounds.
- When the ILUV method was applied to humic substances, recoveries of 100% to 126% were obtained which were also comparable to those obtained with other techniques.
- These findings indicate that the ILUV method developed in this study is a simple,

relatively inexpensive and promising method for determination of DON in natural waters. Testing of natural water samples is needed for further development and validation of the method.

Acknowledgements

This work was supported in part by a Research Grant (R-828-045-01-0) from the United States Environmental Protection Agency's Science to Achieve Results (STAR) program (Office of Research and Development, National Center for Environmental Research and Quality); however, it has not been subjected to the Agency's peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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